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TITLE: Fuel cell electrode substrate incorporating separator as an intercooler and process for preparation thereof

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INVENTOR-INFORMATION:

| NAME | CITY | STATE | ZIP CODE | COUNTRY |
|---|---|---|---|---|
| Shigeta; Masatomo | Iwaki | N/A | N/A | JPX |
| Fukuda; Hiroyuki | Iwaki | N/A | N/A | JPX |
| Kaji; Hisatsugu | Iwaki | N/A | N/A | JPX |
| Saitoh; Kuniyuki | Abiko | N/A | N/A | JPX |

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CLAIMS:

What is claimed is:

1. In a process for producing an electrode substrate for fuel cells comprising (1) two porous carbonaceous layers, each having a number of elongated holes for feeding reactant gases into a fuel cell which holes are defined near the center of the thickness thereof, and (2) a gas impermeable, carbonaceous separator interposed between said layers,

which process comprises (1) supplying, into a mold having a proper configuration, (i) materials for porous layer each of which is a mixture comprising 10-50% by weight of a filler (A), 20-40% by weight of a binder (B) and 20-50% by weight of a pore regulator (C), (ii) a material for forming the elongated holes for feeding reactant gases and (iii) a material for the separator, (2) press molding the thus supplied materials at a temperature in the range of from 70.degree. to 170.degree. C. and a pressure in the range of from 5 to 100 kg/cm.sup.2 for a time period in the range of from 10 to 60 minutes, (3) postcuring the press molded materials at the molding temperature for at least 2 hours and (4) calcining the postcured materials under an inert atmosphere at a temperature in the range of from 800.degree. to 3,000.degree. C.,

the filler (A) being selected from the group consisting of short carbon fibers and carbon particles, the short carbon fiber having a diameter in the range of from 5 to 30 .mu.m, a length in the range of from 0.02 to 2 mm, and a linear carbonizing shrinkage in the range of not more than 3.0% when calcined at 2,000.degree. C.,

the binder (B) being selected from the group consisting of phenol resins, epoxy resins, petroleum and/or coal pitches and mixtures thereof, and having a carbonizing yield in the range of from 30 to 75% by weight,

the pore regulator (C) comprising organic granules, 70% or more of which have a particle diameter in the range of from 30 to 300 .mu.m, the organic granule being selected from the group consisting of polyvinyl alcohols, polyvinyl chlorides, polyethylenes, polypropylenes, polystyrenes and mixtures thereof,

the material (ii) for forming elongated holes for feeding reactant gases being a polymer which does not evaporate nor melt-flow at 100.degree. C., the polymer being selected from the group consisting of polyethylenes, polypropylenes, polystyrenes, polyvinyl alcohols and polyvinyl chlorides, having a carbonizing yield of 30% by weight or less and being (1) a textile fabric of the polymer

comprising single strand or bundles of a number of strands which have been textured, the strand or the bundle having a diameter in the range of from 0.5 to 3.3 mm, the distance between two strands or bundles parallel to the gas flow direction being in the range of from 1.5 to 5 mm and the distance between two strands or bundles perpendicular to the gas flow direction being in the range of from 5 to 50 mm, or (2) a grating-like shaped article of the polymer prepared by extrusion molding of a melt of the polymer into a die or by press molding of pellets or powder of the polymer in a mold, the gratings having a diameter or equivalent diameter in the range of from 0.5 to 3.3 mm, the distance between two gratings parallel to the gas flow direction being in range of from 1.5 to 5 mm and the distance between two gratings perpendicular to the gas flow direction being in the range of from 5 to 50 mm,
the materials for forming elongated holes for feeding reactant gases being each supplied into the mold so that the elongated holes for feeding reactant gases are parallel to each other and to the electrode surface and one side surface of the electrode, are continuously elongated in the porous layer from one of the other side surfaces to another surface opposite thereto, and the elongated holes in the porous layer on one side of the separator and those in the porous layer on the other side of the separator have the directions perpendicular to one another,
wherein the improvements comprise the process comprising the steps of:
(a) supplying, into the mold having a proper configuration, the material for separator, the material for forming elongated holes for flowing coolant which material is a polymer, and the material for separator, in this order and press molding, or further, after press molding, postcuring and calcining,
the material for separator comprising (i) 50-90% by weight of a filler of carbon particles having a diameter of 50 .mu.m or less and (ii) 10-50% by weight of a thermosetting resin binder; and
(b) supplying, into the mold having a proper configuration, the material for porous layer, the material for forming elongated holes for feeding reactant gases, the material for porous layer, the shaped separator by press molding or the calcined separator prepared in the step (a), the material for porous layer, the material for forming elongated holes for feeding reactant gases, and the material for porous layer, in this order, press molding, postcuring, and calcining the postcured materials to integrate the materials as a whole body to obtain an electrode substrate provided with an intercooler,
where (1) said separator has a number of elongated holes for flowing coolant which are constructed from said separator and provided near the center of the thickness in the separator, and which holes are parallel to each other and to the electrode surface and one side surface of the electrode, are continuously elongated in the separator from one of the side surfaces to another side surface opposite thereto, and have a diameter or equivalent diameter in the range of from 2 to 10 mm, and
(2) said separator excluding the elongated holes for flowing coolant has an average bulk density of 1.2 g/cm.sup.3 or more, a specific gas permeability of 1.times.10.sup.31 4 cm.sup.2 /hr.mmAq. or less, a thermal conductivity of 1 kcal/m.hr..degree.C. or more, and a volume resistivity of 10.times.10.sup.-3 .OMEGA..cm or less.
2. In a process for producing an electrode substrate for fuel cells comprising (1) two porous carbonaceous layers, each having a number of elongated holes for feeding reactant gases into a fuel cell which holes are defined near the center of the thickness thereof, and (2) a gas impermeable, carbonaceous separator interposed between said layers,
which process comprises (1) supplying, into a mold having a proper configuration, (i) materials for porous layer each of which is a mixture comprising a filler (A), a binder (B) and a pore regulator (C), (ii) a material for forming the elongated holes for feeding reactant gases and (iii) a material for the separator, (2) press molding the thus supplied materials, (3) postcuring the press molded materials at the molding temperature for at least 2 hours and (4) calcining the postcured materials under an inert atmosphere at a temperature in the range of from 800.degree. to 3,000.degree. C.,
the filler (A) being selected from the group consisting of short carbon fibers and carbon particles,
the binder (B) being selected from the group consisting of phenol resins, epoxy resins, petroleum and/or coal pitches and mixtures thereof, and having a carbonizing yield in the range of from 30 to 75% by weight,
the pore regulator (C) comprising organic granules, the organic granule being selected from the group consisting of polyvinyl alcohols, polyvinyl chlorides, polyethylenes, polypropylenes, polystyrenes and mixtures thereof,

the material (ii) for forming elongated holes for feeding reactant gases being a polymer which does not evaporate nor melt-flow at 100.degree. C., the polymer being selected from the group consisting of polyethylenes, polypropylenes, polystyrenes, polyvinyl alcohols and polyvinyl chlorides, having a carbonizing yield of 30% by weight or less and being (1) a textile fabric of the polymer comprising single strand or bundles of a number of strands which have been textured, the strand or the bundle having a diameter in the range of from 0.5 to 3.3 mm, the distance between two strands or bundles parallel to the gas flow direction being in the range of from 1.5 to 5 mm and the distance between two strands or bundles perpendicular to the gas flow direction being in the range of from 5 to 50 mm, or (2) a grating-like shaped article of the polymer prepared by extrusion molding of a melt or the polymer into a die or by press molding of pellets or powder of the polymer in a mold, the gratings having a diameter or equivalent diameter in the range of from 0.5 to 3.3 mm, the distance between two gratings parallel to the gas flow direction being in the range of from 1.5 to 5 mm and the distance between two gratings perpendicular to the gas flow direction being in the range of from 5 to 50 mm,
the materials for forming elongated holes for feeding reactant gases being each supplied into the mold so that the elongated holes for feeding reactant gases are parallel to each other and to the electrode surface and one side surface of the electrode, are continuously elongated in the porous layer from one of the other side surfaces to another surface opposite thereto, and the elongated holes in the porous layer on one side of the separator and those in the porous layer on the other side of the separator have the directions perpendicular to one another,
wherein the improvements comprise the process comprising the steps of:
(a) supplying, into a mold having a proper configuration, a material for separator, a material for forming elongated holes for flowing coolant which material is a polymer, and a material for separator, in this order and press molding, or further, after press molding, postcuring and calcining,
the material for separator comprising (i) 50-90% by weight of filler of carbon particles having a diameter of 50 .mu.m or less and (ii) 10-50% by weight of a thermosetting resin binder, and
(b) supplying, into a mold having a proper configuration, a material for a more porous layer, the material or forming elongated holes for feeding reactant gases, a material for a less porous layer, the shaped separator by press molding or the calcined separator prepared in the step (a), the material for a less porous layer, the material for forming elongated holes for feeding reactant gases, and the material for a more porous layer, in this order,
the material for a more porous layer being a mixture comprising 10-50% by weight of the filler (A), 20-40% by weight of the binder (B) and 20-50% by weight of the pore regulator (C), and the material for a less porous layer being a mixture comprising 30-70% by weight of the filler (A), 20-40% by weight of the binder (B) and 10-30% by weight of the pore regulator (C), and
press molding, postcuring, and calcinating the postcured materials to integrate the materials as a whole body to obtain an electrode substrate provided with an intercooler,
wherein (1) each of the porous layers comprises a more porous layer, a less porous layer and elongated holes for feeding reactant gases provided between said more porous layer and said less porous layer, and less porous layer having a bulk density larger than that of the more porous layer,
the more porous layer having an average bulk density in the range of from 0.4 to 0.8 g/cm.sup.3, a porosity in the range of from 50 to 80%, a specific gas permeability of 20 ml/cm.hr.mmAq. or more and a thermal conductivity of 0.7 kcal/m.hr..degree.C. or more; and 60% or more of open pores thereof having a diameter of 100 .mu.m or less,
the less porous layer having an average bulk density in the range of from 0.5 to 1.0 g/cm.sup.3 and a thermal conductivity of 0.9 kcal/m.hr..degree.C. or more,
the thickness of said more porous layer being in the range of about a fiftieth to a half of the total thickness of said porous carbonaceous layer,
(2) said separator has a number of elongated holes for flowing coolant which are constructed from said separator and provided near the center of the thickness in the separator, and which holes are parallel to each other and to the electrode surface and one side surface of the electrode, are continuously elongated in the separator from one of the side surfaces to another side surface opposite thereto, and have a diameter or equivalent diameter in the range of from 2 to 10 mm, and
(3) said separator excluding the elongated holes for flowing coolant has an

average bulk density of 1.2 g/cm.sup.3 or more, a specific gas permeability of 1.times.10.sup.-4 cm.sup.2 /hr.mmAq. or less, a thermal conductivity of 1 kcal/m.hr..degree.C. or more, and a volume resistivity of 10.times.10.sup.-3 .OMEGA..cm or less.

3. In a response for producing an electrode substrate for fuel cells comprising (1) two porous carbonaceous layers, each having a number of elongated holes for feeding reactant gases into a fuel cell which holes are defined near the center of the thickness thereof, and (2) a gas impermeable, carbonaceous separator interposed between said layers,

which process comprises (1) supplying, into a mold having a proper configuration, (i) materials for porous layer each of which is a mixture comprising a filler (A), a binder (B) and a pore regulator (C), (ii) a material for forming the elongated holes for feeding reactant gases and (iii) a material for the separator, (2) press molding the thus supplied materials, (3) postcuring the press molded materials at the molding temperature for at least 2 hours and (4) calcining the postcured materials under an inert atmosphere at a temperature in the range of from 800.degree. to 3,000.degree. C.,

the filler (A) being selected from the group consisting of short carbon fibers and carbon particles,

the binder (B) being selected from the group consisting of phenol resins, epoxy resins, petroleum and/or coal pitches and mixtures thereof, and having a carbonizing yield in the range of from 30 to 75% by weight,

the pore regulator (C) comprising organic granules, the organic granule being selected from the group consisting of polyvinyl alcohols, polyvinyl chlorides, polyethylenes, polypropylenes, polystyrenes and mixtures thereof,

the material (ii) for forming elongated holes for feeding reactants gases being a polymer which does not evaporate nor melt-flow at 100.degree. C., the polymer being selected from the group consisting of polyethylenes, polypropylenes, polystyrenes, polyvinyl alcohols and polyvinyl chlorides, having a carbonizing yield of 30% by weight or less and being (1) a textile fabric of the polymer comprising single strand or bundles of a number of strands which have been textured, the strand or the bundle having a diameter in the range of from 0.5 to 3.3 mm, the distance between two strands or bundles parallel to the gas flow direction being in the range of from 1.5 to 5 mm and the distance between two strands or bundles perpendicular to the gas flow direction being in he range of from 5 to 50 mm, or (2) a grating-like shaped article of the polymer prepared by extrusion molding of a melt of the polymer into a die or by press molding of pellets or powder of the polymer in a mold, the gratings having a diameter or equivalent diameter in the range of from 0.5 to 3.3 mm, the distance between two gratings parallel to the gas flow direction being in the range of from 1.5 to 5 mm and the distance between two gratings perpendicular to the gas flow direction being in the range of from 5 to 50 mm,

the materials for forming elongated holes for feeding reactant gases being each supplied into the mold so that the elongated holes for feeding reactant gases are parallel to each other and to the electrode surface and one side surface of the electrode, and continuously elongated in the porous layer from one of the other side surfaces to another surface opposite thereto, and the elongated holes in the porous layer on one side of the separator and those in the porous layer on the other side of the separator have the directions perpendicular to one another,

wherein the improvements comprise the process comprising the steps of:

(a) supplying, into a molding having a proper configuration, a material for separator, a material for forming elongated holes for flowing coolant which material is a polymer, and a material for separator, in this order and press molding, or further, after press molding, postcuring and calcining,

the material for separator comprising (i) 50-90% by weight of a filler of carbon particles having a diameter of 50 .mu.m or less and (ii) 10-50% by weight of a thermosetting resin binder;

(b) supplying into a mold having a proper configuration, a material for a less porous layer, a material for forming elongated holes for feeding reactant gases, and a material for a more porous layer, in this order, press molding, and repeating the above procedures to prepare another same product,

the material for a more porous layer being a mixture comprising 10-50% by weight of the filler (A), 20-40% by weight of the binder (B) and 20-50% by weight of the pore regulator (C) and the material for a less porous layer being a mixture comprising 30-70% by weight of the filler (A), 20-40% by weight of the binder (B) and 10-30% by weight of the pore regulator (C), and

(c) placing, into a mold having a proper configuration, the pressed porous product prepared in the step (b) with the more porous layer being on lower

side, the shaped separator by press molding or the calcined separator prepared in the step (a), and the another pressed porous produce prepared in the step (b) with the less porous layer being faced onto the separator, press molding, postcuring, and calcining the postcured materials to integrate the materials as a whole body to obtain an electrode substrate provided with an intercooler, wherein (1) each of the porous layers comprises a more porous layer, a less porous layer and elongated holes for feeding reactant gases provided between said more porous layer and said less porous layer, the less porous layer having a bulk density larger than that of the more porous layer,
the more porous layer having an average bulk density in the range of from 0.4 to 0.8; g/cm.sup.3, a porosity in the range of from 50 to 80%, a specific gas permeability of 20 ml/cm.hr.mmAq. or more and a thermal conductivity of 0.7 kcal/m.hr..degree.C. or more; and 60% or more of open pores thereof having a diameter of 100 .mu.m or less,
the less porous layer having an average bulk density in the range of from 0.5 to 1.0 g/cm.sup.3 and a thermal conductivity of 0.9 kcal/m.hr..degree.C. or more,
the thickness of said more porous layer being in the range of about a fiftieth to a half of the total thickness of said porous carbonaceous layer,
(2) said separator has a number of elongated holes for flowing coolant which are constructed from said separator and provided near the center of the thickness in the separator, and which holes are parallel to each other and to the electrode surface and one side surface of the electrode, are continuously elongated in the separator from one of the side surfaces to another side surface opposite thereto, and have a diameter or equivalent diameter in the range of 2 to 10 mm, and
(3) said separator excluding the elongated holes for flowing coolant has an average bulk density of 1.2 g/cm.sup.3 or more, a specific gas permeability of 1.times.10.sup.-4 cm.sup.2 /hr.mmAq. or less, a thermal conductivity of 1 kcal/m.hr..degree.C. or more, and a volume resistivity of 10.times.10.sup.-3.sub.x. cm or less.
4. The process of any one of claims 1 to 3, wherein the binder used in the material for separator is a phenol resin.
5. The process of any one of claims 1 to 3, wherein the material for forming elongated holes for flowing coolant is a polymer which does not evaporate nor melt-flow at 100.degree. C.
6. The process of claim 5, wherein the polymer is selected from the group consisting of polyethylenes, polypropylenes, polystyrenes, polyvinyl alcohols and polyvinyl chlorides, and has a carbonizing yield of 30% by weight or less.
7. The process of claim 5, wherein the material or forming elongated holes for flowing coolant is a textile fabric or grating-like shaped article of the polymer.
8. The process of claim 7, wherein the textile fabric comprises single strand or bundles of a number of strands which have been textured and the strand or the bundle has a diameter in the range of from 2.2 to 11 mm.
9. The process of claim 8, wherein the distance between two strands or bundles parallel to the coolant flow direction is in the shape of from 3 to 30 mm and the distance between two strands or bundles perpendicular to the coolant flow direction is in the range of from 5 to 100 mm.
10. The process of claim 7, wherein the grating-like shaped article is prepared by extrusion molding a melt of the polymer in a mold or by press molding of pellets or powder of the polymer in a mold, and the grating have a diameter or equivalent diameter in the range of from 2.2 to 11 mm.
11. The process of claim 10, wherein the distance between two gratings parallel to the coolant flow direction is in the range of from 3 to 30 mm and the distance between two gratings perpendicular to the coolant from direction is in the range of them 5 to 100 mm.
12. The process of any one of claims 1 to 3, wherein the press molding in the step (as) carried out at a temperature in the range of from 120.degree. to 160.degree. and a pressure in the range of from 2 to 150 kg/cm.sup.2 for a time period in the range of from 10 to 60 minutes.
13. The process of any one of claims 1 to 3, wherein the postcuring in the step (a) is carried out at the molding temperature for at least 2 hours.
14. The process of any one of claims 1 to 3, wherein the calcination in the step (a) is carried out under an inert environment at a temperature in the range of from 800.degree. to 3,000.degree. C. for about one hour.
15. The process of claim 1 or 2, wherein the calcination in the step (b) is carried out under an inert environment at a temperature in the range of from 800.degree. to 3,000.degree. or about one hour.

16. The process of claim 3, wherein the press molding in the step (b) is carried out at a temperature in the range of from 60.degree. to 100.degree. C. and a pressure in the range of from 20 to 50 kg/cm.sup.2 for a time period in the range of from 10 to 30 minutes.
17. The process of claim 3, wherein the postcuring in the step (c) is carried out at the molding temperature for at least 2 hours.
18. The process of claim 3, wherein the calcination in the step (c) is carried out under an inert environment at a temperature in the range of from 800.degree. to 3,000.degree. C. for about one hour.
19. The process of any one of claims 1 to 3, wherein the step (a) further comprises: (i) supplying, into a mold having a proper configuration, (1) the mixed material for separator, (2) the material for forming elongated holes for flowing coolant, and (3) the mixed material for separator, in this order; (ii) pre-pressing to prepare a shaped product for a separator plate; (iii) repeating almost the same procedures to prepare four shaped plates for peripheral sealing members; (iv) placing the product for the separator plate prepared in the step (ii) and the plate for the peripheral sealing members prepared in the step (iii) in a mold having a proper configuration; (v) press molding; (vi) postcuring; and (vii) calcining at a temperature of 1,000.degree. C. or higher to form the calcined separator comprising a gas impermeable, carbonaceous separator plate and two pairs of gas impermeable, carbonaceous peripheral sealing members.
20. The process of claim 19, wherein the pre-pressing (ii) is carried out at a temperature in the range of from 70.degree. to 170.degree. C. and a pressure in the range of from 2 to 150 kg/cm.sup.2 for a time period of from 10 to 60 minutes.
21. The process of claim 19, wherein the press molding (v) is carried out at a temperature in the range of from 120.degree. to 170.degree. C. and a pressure in the range of from 2 to 150 kg/cm.sup.2 for a time period of 10 to 20 minutes.
22. The process of claim 19, wherein the post-curing (vi) is carried out at a temperature of 130.degree. to 160.degree. C. and a pressure of 0.5 kg/cm.sup.2 or lower for at least 2 hours.
23. The process of any one of claims 1 to 3, wherein the filler in the material for separator is selected from the group consisting of calcined pieces of oxidized pitch, carbon fiber pieces, graphite particles and calcined phenol particles.